Abiogenic Synthesis in the Martian Environment

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At the spring meeting of the National Academy of Sciences, a committee of the Space Science Board took the following position:[1] "The biological exploration of Mars is a scientific undertaking of the greatest validity and significance. Its realization will be a milestone in the history of human achievement. Its importance and the consequences for biology justify the highest priority among all objectives in space science -- indeed in the space program as a whole."

The Martian environment is hostile to both life and organic chemicals. Intense ultraviolet light, of 2000 A^o wave length, which destroys both life and many chemicals penetrates to the surface of the nearly dry planet.[2] Ozone formed as a result of action of ultraviolet light is in contact with the planetary surface.[3] Even more destructive is the combination of radiation excitation and chemical attack. Certain porphyrins can survive for 400 million years in a reducing environment in the dark. In visible light, in the presence of oxygen, they are destroyed in a few hours.

Mars is extremely dry. Water content of the total atmospheric column is only 0.001 g/cm^2.[4] Life cannot function in such an arid environment.[5,6] Lederberg and Sagan[7] have attempted to minimize the water problem by suggesting that water might be available at local hot spots. Evidence from Mariner 4[8] makes this suggestion appear unsound. Mars does not show evidence of tectonic activity usually associated with hot springs. Under the small atmospheric pressure of Mars, water would boil at about 10°C. The presence of dust storms on Mars indicates high wind velocities and consequent large rates of evaporation from any pool of water near its boiling temperature.

In order to create life it is necessary abiologically first to synthesize at least some organic chemicals. In this paper I will present

new data that makes it unlikely that organic chemicals are being formed on Mars or have been synthesized there in the past. I will describe some experiments which indicate that abiogenic synthesis must be conducted in a highly reducing environment. Mars with its low mass loses hydrogen quickly and the necessary reducing environment to permit synthesis is not present now nor is it likely to have been present for long in the past. Mars has a mass 0.108 that of Earth. Correspondingly, the escape velocity from the surface of Mars is 5.0 km/sec while that from Earth is 11.2 km/sec. Near Earth the presence of a magnetic field tends to prevent escape of ionized particles. No such barrier is associated with Mars.[9]

The Miller[10] experiments of ten years ago, which produced amino acids from methane, ammonia and water, have been hailed as demonstrating that the creation of life on Earth was inevitable. Examination of Miller's papers shows that the results also provide an implicit warning that the creation of life on Mars would not be easy. While creating small amounts of amino acids the irradiation produced larger amounts of other substances including hydrogen. Some of the products of the experiment are shown in Table 1.

In Miller's experiments the hydrogen was retained in his apparatus. On Mars the hydrogen would escape as it was formed. Any original methane-ammonia mixture would be quickly changed to a more oxidized gas.

In the new experiments a series of mixtures of CO_2, N_2, H_2O and H_2 have been studied. The experiments show that large amounts of hydrogen must be present in order to obtain appreciable quantities of amino acids. The major amino acid was glycine. The results are presented in Table 2.

At first sight it is surprising that such high proportions of hydrogen must be present to achieve synthesis of amino acids. However, consideration of some of the photochemistry involved makes the results seem reasonable. In comparison with other molecules, molecular hydrogen is relatively inert to ultraviolet radiation.

In the real situation on Mars, this relative inertness of hydrogen has special significance because of the spectral distribution of solar radiation. The effective wave lengths[11] for reactions and the corresponding energies[12] available are shown in Table 3.

¶ Perusal of Steacie's[13] books on atomic and free radical reactions yields the further generalization that organic compounds containing hydrogen are much easier to split than is elemental hydrogen.

I will now present arguments that the Mars atmosphere was probably never sufficiently reducing for abiogenic synthesis to occur and at most that the atmosphere might have been adequately reducing for a very short time.

To provide a background for discussion of the Martian environment, I will briefly review some facets of Earth history. Most geochemists accept the view advanced by Rubey[14] and others that chemicals in the Earth's atmosphere and oceans are a product of outgassing of the interior of the planet a process which continues today. Rubey estimated that during the planet's history the following amounts per cm^2 of volatiles have appeared at the surface: H_2O, 3.2×10^5 g; CO_2, 1.8×10^4 g; and N_2, 8×10^2 g. The gases were accompanied by an equivalent reducing capacity of 4×10^2 g. H_2.

In the early history of Earth the atmosphere was probably quite reducing. Carbon dioxide issuing from volcanoes quickly dissolved in the oceans where it combined with alkaline substances brought in by weathering of land. Gases such as CO and H_2 and the N_2 tended to remain in the atmosphere. Solar radiation produced more complicated molecules. These dissolved in the oceans, where they could be shielded from ultraviolet radiation. In such a benign environment many organic chemicals can survive millions of years, permitting slow accumulation.

On Mars the sequence of events has been different. Only small amounts of volatile substances have reached the atmosphere which could not be highly reducing by reason of H_2 escape.

The most telling argument against an initial dense atmosphere on our planet, reflecting cosmic abundances of the elements, is the comparative absence of krypton and xenon in the present atmosphere. Mars, with its light mass, must have been even less effective than earth in holding volatile substances. Today Mars cannot retain atomic oxygen. During the process of its formation when gravitational attraction was even less, it could not have retained methane. The present atmosphere of Mars must have been derived largely from two sources: (1) outgassing associated with localized heat generated by meteorite impact, or (2) a mild degree of planetary outgassing. Either process would bring volatiles to the surface gradually. Their composition would resemble those which appeared at the surface of Earth.

An estimate of the amount of volatiles which have reached the surface of Mars can be obtained by considering the fate of nitrogen. On Earth almost all the nitrogen which has reached the surface is now in the atmosphere. Actually, nitrogen has not yet been detected on Mars. The only gases definitely known to be in the Martian atmosphere are water vapor, 0.001 g/cm^2, and carbon

dioxide, 12.0 g/cm^2.[15] The presence of nitrogen is assumed in order to account

for the total pressure of the atmospheres. Kuiper[15]
estimates that the unknown gas involved represents 10 g/cm^2. If all of this is

assumed to be nitrogen the quantity is small in comparison to that on Earth,

and it indicates that Mars has not been outgassed to a degree comparable to

that of Earth. The Mariner 4 pictures are in accord with this view, for they

show no evidence of the tectonic activity which accompanies outgassing.

Another factor affecting Martian history is the small amount of

thermal energy reaching the planet. Mars is 1.52 times farther away from the

sun than is Earth and accordingly receives only 43% as much radiation. As a

result, the average surface temperature of Mars is 30-40°K lower than Earth.[5]

Correspondingly, the humidity of the atmosphere is so low that rain does not
[16]
fall. Without rain and weathering, the mechanisms for absorption of CO_2 would

be ineffective. Hence the present amount of CO_2 in the Martian atmosphere may

approach the total that has ever reached the surface.

A small amount of water is present on Mars. Does it represent the

last residual of water that arrived at the surface countless years ago? Prob-

ably not. The H_2O now present may be due to the solar wind. In one year about

10^{15} atoms/cm^2 of hydrogen strike the Mars atmosphere. There are now about 2 x 10^{19}

atoms of hydrogen per cm^2 of Mars. The present Martian water could be the result

of a transient equilibrium with the contribution of the solar wind balancing

the present escape rate.

One of the crucial facts about Mars is the small amount of chemicals

in the atmosphere in terms of amounts of solar radiation. Suppose that all the

hypothetical nitrogen on Mars was initially present as ammonia. This would

amount to about 4 x 10^{23} molecules per cm^2. If the outgassing process required

10^9 years, the annual production would be 4 x 10^{14} cm^2. Each cm^2 of Mars each

year receives 10^{21} quanta of wave length less than 2250 Å. Thus if all nitrogen arrived as ammonia and at one time (a most unlikely combination of events), solar radiation would destroy it in a time of the order of a thousand years. Alternatively, if the ammonia were produced gradually, each molecule would be greeted by more than 10^6 quanta capable of destroying it. The process would be irreversible for the product, inert hydrogen, would be quickly lost. Similar arguments can be applied to consideration of the fate of any water or methane which might have appeared on Mars. The combination of solar radiation and ease of hydrogen escape have acted to produce and maintain on Mars an environment unsuitable for abiogenic synthesis.

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Table 1

Products Formed
Miller Experiment   1955

Glycine	47 mg.
Alanine	30
CO	420
N_2	210
H_2	161
CO_2	100

The reaction mixture contained 532 mg. C and the yield of glycine based on carbon was 2.8%.

Table 2

Products of Irradiation of Gas Mixtures

Starting Gases, cm. Hg				Percent Carbon Fixed	
CO_2	N_2	H_2O	H_2	Total Carbon	As Glycine
12	6	2.5		0.2	<0.001
12	6	2.5	6	0.3	<0.005
12	6	2.5	12	0.8	0.005
12	6	2.5	18	2.2	0.02
12	6	2.5	24	8.0	0.3
12	6	2.5	36	20	1
6	3	2.5	38	45	2

A two-day irradiation was conducted in an apparatus similar to that of Miller. Volume of the irradiation flask was 1 liter. The final reaction mixture was hydrolyzed overnight with 6 n HCl. Glycine was determined in an amino acid analyzer.

Table 3

Thresholds for Photolysis and Energy Available

Substance	Effective Threshold A°	Solar Energy At $\lambda <$ Threshold ergs cm^{-2} sec^{-1}
NH_3	2250	300
H_2O	1850	42
CO_2	1690	12
CO	1545	5
N_2	1100	0.87
H_2	900	< 0.6